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A Solution of the Equations of Statistical Mechanics

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Abstract

The solution of the initial value problem for Bogoliubov's functional differential equation of non-equilibrium statistical mechanics is obtained. This solution is then expanded in an infinite power series in the density which has the advantage that the calculation of the leading terms requires the solution of s-body problems only for small values of s. A derivation of the equilibrium equation by reduction from the non-equilibrium equation is included.

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1. Introduction.

The statistical mechanical treatment of a classical many-body system usually begins with an 'n-particle density function', D_n , which is the solution of an initial value problem for Liouville's equation. There are, however, two major difficulties with this approach:

1. In the problems of interest the solution of Liouville's equation is equivalent to the solution of an n-body problem where n is very large, and is therefore not practical.

2. The initial conditions are, in general, unknown.

In an attempt to circumvent these difficulties, one introduces 's-particle density functions', F_s , defined by appropriate integrals of D_n . N.N. Bogoliubov has shown ^[1] that for these functions, the Liouville equation can be replaced by a functional differential equation for a generating functional $L[u]$ which generates the functions F_s , and has obtained an expansion of the solution of the equation to first order in the density.

In Section 2 of this paper we derive the functional differential equation by a slight variation of Bogoliubov's method. The resulting equation (20) differs slightly from, but is equivalent to, the equation of Bogoliubov; however, the form of (20) facilitates a new method of solution.

Section 3 contains the main result of this paper. In that section we obtain the solution of the initial value problem for (20) by a method similar to the method devised by B. Zumino ^[4] for the equilibrium case. The solution is then expanded in an infinite power series in the density. In this form, it has the advantage that for small densities it may be approximated by a few terms of the expansion. Then to obtain an explicit expression for F_s where s is small, only certain k-body problems, where k is small, need to be solved. Furthermore only the initial data for certain functions F_j , where j is small, are required. If these data are known, our expansion circumvents both of the difficulties enumerated above.

Sections 4 and 5 are included for the sake of completeness. In Section 4 we carry out a suggestion of Zumino and derive the functional differential equation for the equilibrium case by reduction from the non-equilibrium equation. In Section 5 we solve the equilibrium equation by a slight simplification of Zumino's method.

2. Derivation of the Functional Differential Equation.

We consider a classical mechanical system of n identical monatomic particles contained in a finite volume, V . The dynamical state of the j -th particle is described by the 6 component vector $x_j = (q_j, p_j) = (q_j^1, q_j^2, q_j^3, p_j^1, p_j^2, p_j^3)$ where the q_j^α are the cartesian coordinates of the particle, and the p_j^α are the conjugate momenta. x_j is a point in the phase-space \mathcal{O}_V defined by the restriction that q_j is a point in the finite volume V . The Hamiltonian of the system is given by

$$(1) \quad \mathcal{H}_n = \sum_{i=1}^n h(x_i) + U_n,$$

$$(2) \quad h(x_i) = T(p_i) + u_V(q_i),$$

$$(3) \quad U_n = \sum_{1 \leq i < j \leq n} \phi(|q_i - q_j|),$$

$$(4) \quad T(p_i) = \frac{p_i^2}{2m} = \sum_{\alpha=1}^3 \frac{(p_i^\alpha)^2}{2m},$$

where m denotes the mass of a particle, ϕ is the inter-particle potential and $u_V(q_i)$ is the potential due to the containing boundary. Thus $u_V(q)$ is constant inside V and rapidly approaches infinity at the boundary.

The statistical-mechanical behavior of the system is described by the n-particle 'probability density' function, $D_n(t, x_1, \dots, x_n)$ which is symmetric in the variables (x_1, \dots, x_n) , is normalized by the condition

$$(5) \quad \int_{\Omega_V} D_n dx_1 \dots dx_n = 1 ,$$

and is a solution of Liouville's equation,

$$(6) \quad \frac{\partial D_n}{\partial t} = \left[\mathcal{H}_n; D_n \right] = \sum_{i=1}^n \sum_{\alpha=1}^{\infty} \left\{ \frac{\partial \mathcal{H}_n}{\partial q_i^\alpha} \frac{\partial D_n}{\partial p_i^\alpha} - \frac{\partial \mathcal{H}_n}{\partial p_i^\alpha} \frac{\partial D_n}{\partial q_i^\alpha} \right\} .$$

Let $S_t^{(n)}$ denote the solution operator of the n-particle mechanical system, i.e., if the system at time $t = 0$ is represented by the state $\{x_1, \dots, x_n\}$, at time t it will be represented by the state $\{x'_1, \dots, x'_n\} = S_t^{(n)} \{x_1, \dots, x_n\}$. Under suitable conditions, the solution operator exists, but of course cannot be calculated explicitly except when n is very small. If g is a function of $(\tau, x_1, \dots, x_{n+k})$ it is convenient to define $S_t^{(n)} g$ by the equation

$$(7) \quad S_t^{(n)} g(\tau, x_1, \dots, x_{n+k}) = g(\tau, S_t^{(n)} \{x_1, \dots, x_n\}, x_{n+1}, \dots, x_{n+k}) .^*$$

In terms of the solution operator, one may express the solution of the initial value problem for Liouville's equation in the form

* Thus $S_t^{(n)}$ acts on the first n of the variables x_j appearing in g .

$$(8) \quad D_n(t, x_1, \dots, x_n) = S_{-t}^{(n)} D_n(0, x_1, \dots, x_n).$$

However, since $S_{-t}^{(n)}$ cannot be calculated, and since $D_n(0, x_1, \dots, x_n)$ is in general unknown, the solution (8) is of no practical value.

We introduce the s-particle density functions

$$(9) \quad F_{n,s}(t, x_1, \dots, x_s) = V^s \int_{\Omega_V} D_n(t, x_1, \dots, x_n) dx_{s+1} \dots dx_n;$$

$$s = 0, 1, 2, \dots \quad .$$

It follows that $F_{n,s}$ is symmetric in (x_1, \dots, x_s) , $F_{n,0} = 1$, and

$$(10) \quad \int_{\Omega_V} \frac{1}{V^s} F_{n,s} dx_1 \dots dx_s = \int_{\Omega_V} D_n dx_1 \dots dx_n = 1; \quad s = 1, 2, \dots \quad .$$

We now set $v = \frac{V}{n}$ and introduce the functional

$$(11) \quad L_n[t, u] = \int_{\Omega_V} D_n(t, x_1, \dots, x_n) \prod_{i=1}^n [\bar{1} + vu(x_i)] dx_1 \dots dx_n ,$$

which is defined on the domain of functions $u(x)$ for which the above integral converges. By functional differentiation* we obtain

* See e.g. [5].

$$(12) \quad \frac{\delta^s L_n}{\delta u(x_1) \dots \delta u(x_s)} = \frac{n!}{(n-s)!} \int_V D_n(t, x_1, \dots, x_n) \prod_{i=s+1}^n [1 + u(x_i)] dx_{s+1} \dots dx_n;$$

$$s = 0, 1, 2, \dots, n;$$

$$(13) \quad \left. \frac{\delta^s L_n}{\delta u(x_1) \dots \delta u(x_s)} \right|_{u=0} = \frac{n!}{n^s (n-s)!} F_{n,s}(t, x_1, \dots, x_s); \quad s = 0, 1, 2, \dots, n.$$

With the aid of (13), L_n may now be expressed as a (finite) series expansion around $u = 0$:

$$(14) \quad L_n[t, u] = 1 + \sum_{s=1}^n \frac{1}{s!} (1 - \frac{1}{n}) \dots (1 - \frac{s-1}{n}) \int_V F_{n,s}(t, x_1, \dots, x_s) u(x_1) \dots u(x_s) dx_1 \dots dx_s.$$

A differential equation for L_n may be obtained by multiplying (6) by $\prod_{i=1}^n [1 + vu(x_i)]$ and integrating with respect to x_1, \dots, x_n over \cap_V .

We obtain

$$(15) \quad \frac{\partial L_n}{\partial t} = \sum_{k=1}^n \int_{\cap_V} [1 + vu(x_k)] \left\{ h(x_k); D_n \prod_{\substack{i=1 \\ i \neq k}}^n [1 + vu(x_i)] \right\} dx_1 \dots dx_n$$

$$+ \sum_{1 \leq r < s \leq n} \int_{\cap_V} [1 + vu(x_r)] [1 + vu(x_s)] \left\{ \phi(|q_r - q_s|); D_n \prod_{\substack{i=1 \\ i \neq r, s}}^n [1 + vu(x_i)] \right\} dx_1 \dots dx_n.$$

By making use of the symmetry of D_n (15) becomes

$$(16) \quad \frac{\partial L_n}{\partial t} = n \int_{\cap_V} [1 + vu(x_1)] \left\{ h(x_1); \int_{\cap_V} D_n \prod_{i=2}^n [1 + vu(x_i)] dx_2 \dots dx_n \right\} dx_1$$

$$+ \frac{n(n-1)}{2} \int_{\cap_V} [1 + vu(x_1)] [1 + vu(x_2)] \left\{ \phi(|q_1 - q_2|); \int_{\cap_V} D_n \prod_{i=3}^n [1 + vu(x_i)] dx_3 \dots dx_n \right\} dx_1 dx_2$$

$$= \frac{1}{v} \int_{\cap_V} [1 + vu(x_1)] \left\{ h(x_1); \frac{\delta L_n}{\delta u(x_1)} \right\} dx_1$$

$$+ \frac{1}{2v^2} \int_{\cap_V} [1 + vu(x_1)] [1 + vu(x_2)] \left\{ \phi(|q_1 - q_2|); \frac{\delta^2 L_n}{\delta u(x_1) \delta u(x_2)} \right\} dx_1 dx_2.$$

We now let $n \rightarrow \infty$ and $V \rightarrow \infty$ in (14) and (16) in such a way that $v = \frac{V}{n}$ is finite. If we set

$$(17) \quad L[t, u] = \lim_{\substack{n \rightarrow \infty \\ V \rightarrow \infty}} L_n[t, u]$$

then from (14)

$$(18) \quad L[t, u] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int F_s(t, x_1, \dots, x_s) u(x_1) \dots u(x_s) dx_1 \dots dx_s.$$

Here

$$(19) \quad F_s(t, x_1, \dots, x_s) = \lim_{\substack{n \rightarrow \infty \\ V \rightarrow \infty}} F_{n,s}(t, x_1, \dots, x_s).$$

From (16)

$$(20) \quad \frac{\partial L}{\partial t} = \int \left[u(x_1) + \frac{1}{v} \right] \left[T(p_1); \frac{\delta L}{\delta u(x_1)} \right] dx_1 \\ + \frac{1}{2} \int \left[u(x_1) + \frac{1}{v} \right] \left[u(x_2) + \frac{1}{v} \right] \left[\phi(|q_1 - q_2|); \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} \right] dx_1 dx_2.$$

It follows from (18) that

$$(21) \quad F_s(t, x_1, \dots, x_s) = \left. \frac{\delta^s L}{\delta u(x_1) \dots \delta u(x_s)} \right|_{u=0}.$$

Equation (20) is the functional differential equation which we shall solve in the next section. The solution L is called the 'generating functional' because it generates the functions F_s by means of (21). We have derived (20) by the method of Bogoliubov^[1] with a slight modification, and our equation apparently differs slightly from the corresponding equation (7.9) of [1]. However, the difference is only apparent. The two equations can be shown to be equivalent, and it will be seen that our form is more suggestive of how to proceed in solving the equation.

By applying the operator $\frac{\delta^s}{\delta u(x_1) \dots \delta u(x_s)} \Big|_{u=0}$ to (20) one can obtain the infinite system of equations*

$$(22) \quad \frac{\partial F_s}{\partial t} = [H_s; F_s] + \frac{1}{v} \int \left[\sum_{1 \leq i \leq s} \phi(|q_i - q_{s+1}|); F_{s+1} \right] dx_{s+1}; \quad s = 1, 2, \dots,$$

where

$$(23) \quad H_s = \sum_{i=1}^s T(p_i) + U_s; \quad U_s = \sum_{1 \leq i < j \leq s} \phi(|q_i - q_j|); \quad s = 1, 2, 3, \dots$$

The system (22) is equivalent to the single equation (20).

3. Solution of the Functional Differential Equation.

In order to solve (20) we begin by examining the case of zero density,

$\frac{1}{v} = 0$. We shall use superscripts 'o' to denote this case. Thus**

$$(24) \quad L^o[t, w] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int F_s^o(t, x_1, \dots, x_s) w(x_1) \dots w(x_s) dx_1 \dots dx_s,$$

$$(25) \quad \frac{\partial L^o}{\partial t} - \int w(x_1) \left[T(p_1); \frac{\delta L^o}{\delta w(x_1)} \right] dx_1 - \frac{1}{2} \int w(x_1) w(x_2) \left[\phi(|q_1 - q_2|); \frac{\delta^2 L^o}{\delta w(x_1) \delta w(x_2)} \right] dx_1 dx_2 = 0,$$

$$(26) \quad F_s^o(t, x_1, \dots, x_s) = \frac{\delta^s L^o}{\delta w(x_1) \dots \delta w(x_s)} \Big|_{w=0},$$

and (22) reduces to

$$(27) \quad \frac{\partial F_s^o}{\partial t} = [H_s; F_s^o]; \quad s = 1, 2, \dots$$

The solution of (27) is immediately obtained in terms of the solution operator $S_t^{(s)}$ corresponding to the Hamiltonian, H_s . It is given by

$$(28) \quad F_s^o(t, x_1, \dots, x_s) = S_{-t}^{(s)} F_s^o(0, x_1, \dots, x_s); \quad s = 1, 2, \dots$$

* See e.g. [1].

** It is convenient now to denote the arbitrary testing functions by w instead of u .

Inserting this expression in (24) we obtain the solution of (25) subject to the initial conditions

$$(29) \quad L^0[0, w] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int F_s^0(0, x_1, \dots, x_s) w(x_1) \dots w(x_s) dx_1 \dots dx_s,$$

where the $F_s^0(0, x_1, \dots, x_s)$ are the given initial data.

In order to solve the general equation (20) we observe that the form of the latter suggests that we try a solution of the form

$$(30) \quad L[t, u] = L^0[t, w]; \quad w(x) = u(x) + \frac{1}{v}.$$

$$\text{Then } \frac{\delta L}{\delta u(x_1)} = \frac{\delta L^0}{\delta w(x_1)}, \quad \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} = \frac{\delta^2 L^0}{\delta w(x_1) \delta w(x_2)}, \quad \frac{\partial L}{\partial t} = \frac{\partial L^0}{\partial t}, \quad \text{and inserting}$$

in (20) we see at once that that equation is satisfied by virtue of the fact that L^0 satisfies (25).

But (20) must be solved subject to the initial conditions

$$(31) \quad L[0, u] = \mathcal{L}[u] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int F_s(0, x_1, \dots, x_s) u(x_1) \dots u(x_s) dx_1 \dots dx_s.$$

The functions $F_s(0, x_1, \dots, x_s)$ are the given initial data. In terms of (30) this becomes

$$(32) \quad L^0[0, w] = \mathcal{L}[u]; \quad u = w - \frac{1}{v}.$$

The main result of this paper is the general solution of (20) defined by (30). If $L^0[t, w]$ is the solution of the initial value problem for (25) with initial conditions (32), then $L[t, u]$ is the solution of the initial value problem for the general equation (20) with initial conditions (31).

The method we have used in obtaining this solution closely resembles the method devised by B. Zumino^[4] to solve the corresponding functional differential equation for the equilibrium case. This is discussed in Section 5.

We now proceed to obtain expansions of the functions $F_s(t, x_1, \dots, x_s)$ in powers of the density, $\frac{1}{v}$. For this purpose it is convenient to introduce a functional of two variables

$$(33) \quad Q[t, u, w] = 1 + \sum_{k=1}^{\infty} \frac{1}{k!} \int S_{-t}^{(k)} \frac{\delta^k \mathcal{L}}{\delta u(x_1) \dots \delta u(x_k)} w(x_1) \dots w(x_k) dx_1 \dots dx_k.$$

Now from (24) and (32)

$$F_k^O(0, x_1, \dots, x_k) = \frac{\delta^{k, L^O} [0, w]}{\delta w(x_1) \dots \delta w(x_k)} \bigg|_{w=0} = \frac{\delta^k \mathcal{L}}{\delta u(x_1) \dots \delta u(x_k)} \bigg|_{u=-\frac{1}{v}}.$$

Hence from (28)

$$(34) \quad Q[t, u, w] \bigg|_{u=-\frac{1}{v}} = 1 + \sum_{k=1}^{\infty} \frac{1}{k!} \int F_k^O(t, x_1, \dots, x_k) w(x_1) \dots w(x_k) dx_1 \dots dx_k = L^O[t, w].$$

From (21), (30) and (34)

$$(35) \quad F_s(t, x_1, \dots, x_s) = \frac{\delta^{s, L^O} [t, w]}{\delta w(x_1) \dots \delta w(x_s)} \bigg|_{w=\frac{1}{v}} = \frac{\delta^s Q}{\delta w(x_1) \dots \delta w(x_s)} \bigg|_{w=\frac{1}{v}, u=-\frac{1}{v}}.$$

Now, from (33)

$$(36) \quad \frac{\delta^s Q}{\delta w(x_1) \dots \delta w(x_s)} = \sum_{j=0}^{\infty} \frac{1}{j!} \int S_{-t}^{(j+s)} \frac{\delta^{j+s} \mathcal{L}}{\delta u(x_1) \dots \delta u(x_{j+s})} w(x_{s+1}) \dots w(x_{s+j}) dx_{s+1} \dots dx_{s+j}$$

and from (31)

$$(37) \quad \frac{\delta^{j+s} \mathcal{L}}{\delta u(x_1) \dots \delta u(x_{j+s})} = \sum_{n=0}^{\infty} \frac{1}{n!} \int F_{n+j+s}(0, x_1, \dots, x_{n+j+s})$$

$$\times u(x_{j+s+1}) \dots u(x_{j+s+n}) dx_{j+s+1} \dots dx_{j+s+n}.$$

* This functional is needed in the analysis in order to avoid expressions involving divergent integrals.

We now insert (37) in (36). The resulting double series can be rearranged and evaluated for $u = -w$. We obtain

$$\frac{\delta^s_Q}{\delta w(x_1) \dots \delta w(x_s)} \bigg|_{u=-w} = \sum_{k=0}^{\infty} \int \left[\sum_{j=0}^k \frac{(-1)^{k-j}}{j!(k-j)!} S_{-t}^{(j+s)} F_{k+s}(0, x_1, \dots, x_{k+s}) \right] w(x_{s+1}) \dots w(x_{s+k}) dx_{s+1} \dots dx_{s+k}.$$

Thus from (35)

$$(38) \quad F_s(t, x_1, \dots, x_s) = \sum_{k=0}^{\infty} \left(\frac{1}{v}\right)^k \int \left[\sum_{j=0}^k \frac{(-1)^{k-j}}{j!(k-j)!} S_{-t}^{(j+s)} F_{k+s}(0, x_1, \dots, x_{k+s}) \right] dx_{s+1} \dots dx_{s+k};$$

$$s = 1, 2, \dots$$

This is our expansion of F_s as a power series in the density.

In order to check the results, one can show in a straightforward manner that (38) satisfies the system of equations (22). To verify that the initial conditions are satisfied, we may set $t = 0$ in (38). Since $S_0^{(s)}$ is the identity operator, the integrand in (38) reduces to

$$(39) \quad F_{k+s}(0, x_1, \dots, x_{k+s}) \sum_{j=0}^k \frac{(-1)^{k-j}}{j!(k-j)!}.$$

But

$$(40) \quad \sum_{j=0}^k \frac{(-1)^{k-j}}{j!(k-j)!} = \frac{1}{k!} \sum_{j=0}^k \binom{k}{j} (-1)^{k-j} = \frac{1}{k!} (1-1)^k = 0, \quad \text{for } k = 1, 2, \dots;$$

thus every term in (38) vanishes except the first and the series reduces to $F_s(0, x_1, \dots, x_s)$ as required.

The series expansion (38) is a very useful form of the solution. We observe that for small densities ($\frac{1}{v} \ll 1$), the function F_s is approximated by terminating the series after a few terms. Now the functions F_s of main interest are those for which s is small, and for these functions, the

calculation of the leading terms of the expansion requires a knowledge only of solution operators $S_t^{(k)}$ where k is small and initial data $F_j(0, x_1, \dots, x_j)$ where j is small.

The leading terms of (38) are given by

$$(41) \quad F_S(t, x_1, \dots, x_S) = S_{-t}^{(s)} F_S(0, x_1, \dots, x_S) + \frac{1}{v} \int \left[S_{-t}^{(s+1)} F_{s+1}(0, x_1, \dots, x_{s+1}) - S_{-t}^{(s)} F_{s+1}(0, x_1, \dots, x_{s+1}) \right] dx_{s+1} + O\left(\frac{1}{v^2}\right).$$

In [1], Bogoliubov obtains the equation

$$(42) \quad F_S(t, x_1, \dots, x_S) = S_{-t}^{(s)} F_S(0, x_1, \dots, x_S) + \frac{1}{v} \int_0^t \left\{ S_{\tau-t}^{(s)} \left[\int_{1 \leq i \leq s} \phi(|q_i - q_{s+1}|) S_{-\tau}^{(s+1)} F_{s+1}(0, x_1, \dots, x_{s+1}) \right] dx_{s+1} \right\} d\tau + O\left(\frac{1}{v^2}\right).$$

With a little manipulation it is possible to reduce (42) to the simpler form (41).

4. Derivation of the Equilibrium Equation.

In this section we shall derive the well-known functional differential equation for the equilibrium case by reduction from the general equation (20). The first step is to derive a new form of (20) by expanding the Poisson brackets that appear in that equation (as is done in (6)) and by using the following identity which is obtained by interchanging integration variables:

$$(43) \quad \int \left[u(x_1) + \frac{1}{v} \right] \left[u(x_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_2^\alpha} \frac{\partial}{\partial p_2^\alpha} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} dx_1 dx_2 = \int \left[u(x_1) + \frac{1}{v} \right] \left[u(x_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\partial}{\partial p_1^\alpha} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} dx_1 dx_2.$$

With the aid of (43), (20) now becomes

$$(44) \quad \frac{\partial L}{\partial t} = \sum_{\alpha=1}^3 \left\{ -\frac{1}{m} \int \left[u(x_1) + \frac{1}{v} \right] p_1^\alpha \frac{\partial}{\partial q_1^\alpha} \frac{\delta L}{\delta u(x_1)} dx_1 \right. \\ \left. + \int \left[u(x_1) + \frac{1}{v} \right] \left[u(x_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\partial}{\partial p_1^\alpha} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} dx_1 dx_2 \right\}.$$

Let us now consider time-independent solutions,

$$(45) \quad L[u] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int F_s(x_1, \dots, x_s) u(x_1) \dots u(x_s) dx_1 \dots dx_s.$$

Then $\frac{\partial L}{\partial t} = 0$, and (44) will be satisfied if

$$(46) \quad \sum_{\alpha=1}^3 \left\{ -\frac{1}{m} p_1^\alpha \frac{\partial}{\partial q_1^\alpha} \frac{\delta L}{\delta u(x_1)} + \int \left[u(x_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\partial}{\partial p_1^\alpha} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} dx_2 \right\} = 0.$$

This equation is an identity in $x_1 = (q_1, p_1)$. It is sufficient for (44), but not necessary.

Following a suggestion of Zumino^[4], let us now consider solutions of (46) for which

$$(47) \quad F_s(x_1, \dots, x_s) = c^{-s} \exp \left[-\frac{1}{2m\theta} [p_1^2 + \dots + p_s^2] \right] f_s(q_1, \dots, q_s),$$

where θ is a constant and

$$(48) \quad c = \int \exp \left[-\frac{p^2}{2m\theta} \right] dp.$$

Let $\bar{L}[u]$ denote the restriction of $L[u]$ to the domain of functions $u = u(q)$ which are independent of p . Then if (47) is assumed,

$$(49) \quad L[u] = 1 + \sum_{k=1}^{\infty} \frac{1}{k!} \int f_k(q_1, \dots, q_k) \prod_{i=1}^k c^{-1} \exp \left[\frac{-p_i^2}{2m\theta} \right] u(x_i) dx_1 \dots dx_k$$

and

$$(50) \quad \bar{L}[u] = 1 + \sum_{k=1}^{\infty} \frac{1}{k!} \int f_k(q_1, \dots, q_k) u(q_1) \dots u(q_k) dq_1 \dots dq_k.$$

By functional differentiation of (49) and (50) it is easy to show that

$$(51) \quad \frac{\overline{\delta^s L}}{\delta u(x_1) \dots \delta u(x_s)} = c^{-s} \prod_{i=1}^s \exp \left[-\frac{r_i^2}{2m\theta} \right] \frac{\delta^s L}{\delta u(q_1) \dots \delta u(q_s)},$$

and

$$(52) \quad \frac{\partial}{\partial p_1^\alpha} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} = -\frac{r_1^\alpha}{m\theta} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)}.$$

With the aid of (52), (46) becomes

$$(53) \quad \sum_{\alpha=1}^3 r_1^\alpha \left\{ \frac{\partial}{\partial q_1^\alpha} \frac{\delta L}{\delta u(x_1)} + \frac{1}{\theta} \left[u(x_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\delta^2 L}{\delta u(x_1) \delta u(x_2)} \right\} dx_2 = 0.$$

If we restrict (53) to functions $u = u(q)$ and use (51) we obtain

$$(54) \quad c^{-1} \exp \left[-\frac{r_1^2}{2m\theta} \right] \sum_{\alpha=1}^3 r_1^\alpha \left\{ \frac{\partial}{\partial q_1^\alpha} \frac{\delta L}{\delta u(q_1)} + \frac{1}{\theta} \left[u(q_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\delta^2 L}{\delta u(q_1) \delta u(q_2)} \right. \\ \left. \times \left[c^{-1} \exp \left[-\frac{r_2^2}{2m\theta} \right] dp_2 \right] dq_2 \right\} = 0,$$

and since p_1 is arbitrary,

$$(55) \quad \frac{\partial}{\partial q_1^\alpha} \frac{\delta L}{\delta u(q_1)} + \frac{1}{\theta} \left[u(q_2) + \frac{1}{v} \right] \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\delta^2 L}{\delta u(q_1) \delta u(q_2)} dq_2 = 0; \quad \alpha = 1, 2, 3.$$

(55) is the well-known^{*} equation of equilibrium theory, where $\theta = kT$, k is the Boltzman constant, and T is the absolute temperature. This equation is usually derived from an assumption about the explicit form of D_{11} . This form is given by

* See e.g. [1] or [4].

$$(56) \quad D_n = Z_n^{-1} \exp \left[-\frac{1}{\theta} H_n \right] ; H_n = \sum_{j=1}^n T(p_j) + U_n ; \text{ where}$$

$$(57) \quad Z_n = \int_{\Omega_V} \exp \left[-\frac{1}{\theta} H_n \right] dx_1 \dots dx_n = Q_n c^n ; Q_n = \int_V \exp \left[-\frac{1}{\theta} U_n \right] dq_1 \dots dq_n.$$

The purpose of this section has been to show that the equilibrium equation (55) can be derived from the general equation (20) by using the assumption (47). It is not surprising that this can be done, in view of the fact that (47) is a consequence of (56). To see this, we use (19) and (9) to obtain

$$(58) \quad F_s(t, x_1, \dots, x_s) = \lim_{\substack{n \rightarrow \infty \\ V \rightarrow \infty}} F_{n,s} = \lim_{\substack{n \rightarrow \infty \\ V \rightarrow \infty}} V^s \int_{\Omega_V} Z_n^{-1} \exp \left[-\frac{1}{\theta} H_n \right] dx_{s+1} \dots dx_n \\ = \lim_{\substack{n \rightarrow \infty \\ V \rightarrow \infty}} V^s c^{-s} \exp \left[-\frac{1}{2m\theta} (P_1^2 + \dots + P_s^2) \right] \int_V Q_n^{-1} \exp \left[-\frac{1}{\theta} U_n \right] dq_{s+1} \dots dq_n.$$

From (58) we see at once that (47) follows with

$$(59) \quad f_s(q_1, \dots, q_s) = \lim_{\substack{n \rightarrow \infty \\ V \rightarrow \infty}} V^s \int_V Q_n^{-1} \exp \left[-\frac{1}{\theta} U_n \right] dq_{s+1} \dots dq_n.$$

Before proceeding to the solution of (55) we point out that that equation is also equivalent to an infinite system of equations, given by*

$$(60) \quad \frac{\partial f_k}{\partial q_1^\alpha} + \frac{1}{\theta} \frac{\partial U_k}{\partial q_1^\alpha} f_k + \frac{1}{\theta v} \int \frac{\partial \phi(|q_1 - q_{k+1}|)}{\partial q_1^\alpha} f_{k+1} dq_{k+1} = 0, \quad \alpha = 1, 2, 3; \\ k = 1, 2, \dots$$

* See [1] for the derivation.

5. Solution of the Equilibrium Equation.

In this section we shall solve the equilibrium equation (55) by a slight simplification of a method due to B. Zumino^[4]. As in Section 3 we begin by examining the case of zero density, $\frac{1}{V} = 0$. We again use superscripts 'o' to denote this case. Thus

$$(61) \quad \overline{L^0} [w] = 1 + \sum_{k=1}^{\infty} \frac{1}{k!} \int f_k^o(q_1, \dots, q_k) w(q_1) \dots w(q_k) dq_1 \dots dq_k,$$

$$(62) \quad \frac{\partial}{\partial q_1^\alpha} \frac{\delta \overline{L^0}}{\delta w(q_1)} + \frac{1}{\theta} \int w(q_2) \frac{\partial \phi(|q_1 - q_2|)}{\partial q_1^\alpha} \frac{\delta^2 \overline{L^0}}{\delta w(q_1) \delta w(q_2)} dq_2 = 0; \quad \alpha = 1, 2, 3,$$

$$(63) \quad f_s^o(q_1, \dots, q_s) = \frac{\delta^s \overline{L^0}}{\delta w(q_1) \dots \delta w(q_s)} \Big|_{w=0},$$

and (60) reduces to

$$(64) \quad \frac{\partial f_k^o}{\partial q_1^\alpha} + \frac{1}{\theta} \frac{\partial U_k}{\partial q_1^\alpha} f_k^o = 0; \quad \alpha = 1, 2, 3; k = 1, 2, \dots$$

In order to solve (64), set

$$(65) \quad f_k^o = C_k(q_1, \dots, q_k) \exp \left[-\frac{1}{\theta} U_k \right]; \quad k = 1, 2, \dots$$

From (64),

$$(66) \quad \frac{\partial C_k}{\partial q_1^\alpha} = 0; \quad \alpha = 1, 2, 3; k = 1, 2, \dots$$

Since $C_k(q_1, \dots, q_k)$ is symmetric in its arguments, it follows that C_k is a constant. In order to determine the constant, we observe that by letting $n \rightarrow \infty$, $V \rightarrow \infty$ in (10) we obtain

$$(67) \quad \lim_{V \rightarrow \infty} \frac{1}{V^s} \int_{\Omega_V} F_s dx_1 \dots dx_s = 1.$$

Now from (47)

$$(68) \quad \lim_{V \rightarrow \infty} \frac{1}{V^s} \int_V f_s dq_1 \dots dq_s = 1,$$

and from (65)

$$(69) \quad \lim_{V \rightarrow \infty} \frac{1}{V^s} \int_V \exp \left[-\frac{1}{\theta} U_s \right] dq_1 \dots dq_s = \frac{1}{C_s}.$$

It is clear from (69) that $C_s = 1$ for potentials $\phi(r)$ which vanish sufficiently rapidly as $r \rightarrow \infty$. We shall therefore impose as a condition on ϕ that the left side of (69) be equal to 1 for $s = 1, 2, 3, \dots$. It follows now from (65) that

$$(70) \quad f_k^o(q_1, \dots, q_k) = \exp \left[-\frac{1}{\theta} U_k \right]; \quad k = 1, 2, \dots$$

The solution of (55) for non-zero density can be obtained from the zero density solution in a manner very similar to the procedure used in the non-equilibrium case. We begin with a trial form of the solution slightly more general than the one used in Section 3:

$$(71) \quad \bar{L}[u] = \bar{L}^o[w]; \quad w = a(u + \frac{1}{v}); \quad a = \text{const.}$$

By functional differentiation we have

$$(72) \quad \frac{\delta^s \bar{L}}{\delta u(q_1) \dots \delta u(q_s)} = a^s \frac{\delta^s \bar{L}^o}{\delta w(q_1) \dots \delta w(q_s)}$$

and substituting in (55) we see that the latter equation is satisfied because \bar{L}^o satisfies (62).

In order to determine the constant, a , we observe first that since U_n is a function only of the coordinate differences $(q_1 - q_j)$, (59) implies that $f_1(q_1)$ is a constant, and (68) implies that the constant is unity. Thus

$$(73) \quad f_1(q_1) = 1.$$

Now from (73) and (50) it follows that

$$(74) \quad \left. \frac{\delta \bar{L}}{\delta u(q_1)} \right|_{u=0} = 1; \quad \bar{L}[0] = 1.$$

This in turn implies that

$$(75) \quad a \left. \frac{\delta \bar{L}^0}{\delta w(q_1)} \right|_{w=\frac{a}{v}} = 1; \quad \bar{L}^0 \left[\frac{a}{v} \right] = 1.$$

We shall see that (75) suffices to determine the constant a .

Now from (50) and (72),

$$(76) \quad f_s(q_1, \dots, q_s) = \left. \frac{\delta^s \bar{L}}{\delta u(q_1) \dots \delta u(q_s)} \right|_{u=0} = a^s \left. \frac{\delta^s \bar{L}^0}{\delta w(q_1) \dots \delta w(q_s)} \right|_{w=\frac{a}{v}}.$$

It would appear that we need only differentiate (61) s times and set $w = \frac{a}{v}$ to obtain an explicit formula for $f_s(q_1, \dots, q_s)$. However, this is incorrect because $f_k^0 \approx 1$ for large $|q_1 - q_j|$ and the integrals in (61) converge only for testing functions $w(q)$ which vanish sufficiently rapidly at infinity. For $w = \frac{a}{v}$, the integrals diverge. The difficulty is that (61) does not represent the functional $\bar{L}^0[w]$ in a sufficiently large domain of functions $w(q)$. What is needed is an 'analytic continuation' of the representation of the functional.

Such an analytic continuation can be obtained by the following transformation which was suggested by Zumino^[4].

$$(77) \quad \overline{L}^{\circ}[w] = \exp \left[\overline{M}^{\circ}[w] \right], \quad \overline{M}^{\circ}[w] = \log \overline{L}^{\circ}[w],$$

where

$$(78) \quad \overline{M}^{\circ}[w] = \sum_{k=1}^{\infty} \frac{1}{k!} \left(g_k^{\circ}(q_1, \dots, q_k) w(q_1) \dots w(q_k) d_{q_1} \dots d_{q_k} \right).$$

Now

$$f_1^{\circ}(q_1) = \frac{\delta \overline{L}^{\circ}}{\delta w(q_1)} \Big|_{w=0} = \left[\exp \left[\overline{M}^{\circ}[w] \right] \frac{\delta \overline{M}^{\circ}}{\delta w(q_1)} \right]_{w=0} = \frac{\delta \overline{M}^{\circ}}{\delta w(q_1)} \Big|_{w=0} = g_1^{\circ}(q_1).$$

Proceeding in this manner, we may obtain the following relations between the

f_k° and g_k° :

$$(79) \quad f_1^{\circ}(q_1) = g_1^{\circ}(q_1)$$

$$f_2^{\circ}(q_1, q_2) = g_1^{\circ}(q_1) g_1^{\circ}(q_2) + g_2^{\circ}(q_1, q_2)$$

$$\begin{aligned} f_3^{\circ}(q_1, q_2, q_3) &= g_1^{\circ}(q_1) g_1^{\circ}(q_2) g_1^{\circ}(q_3) + g_2^{\circ}(q_1, q_2) g_1^{\circ}(q_3) + g_2^{\circ}(q_2, q_3) g_1^{\circ}(q_1) \\ &\quad + g_2^{\circ}(q_1, q_3) g_1^{\circ}(q_2) + g_3^{\circ}(q_1, q_2, q_3), \end{aligned}$$

$$(80) \quad g_1^{\circ}(q_1) = f_1^{\circ}(q_1)$$

$$g_2^{\circ}(q_1, q_2) = f_2^{\circ}(q_1, q_2) - f_1^{\circ}(q_1) f_1^{\circ}(q_2)$$

$$\begin{aligned} g_3^{\circ}(q_1, q_2, q_3) &= f_3^{\circ}(q_1, q_2, q_3) - f_1^{\circ}(q_1) f_2^{\circ}(q_2, q_3) - f_1^{\circ}(q_2) f_2^{\circ}(q_1, q_3) - f_1^{\circ}(q_3) f_2^{\circ}(q_1, q_2) \\ &\quad + 2f_1^{\circ}(q_1) f_1^{\circ}(q_2) f_1^{\circ}(q_3), \end{aligned}$$

etc. Functions g_k° related to the f_k° in this manner are known in statistical mechanics as Ursell functions. We observe that except for g_1° they vanish for

large values of $|q_1 - q_j|$.

Let

$$(81) \quad z = \frac{a}{v}.$$

From (77) and (75),

$$(82) \quad \left. \frac{\delta \bar{M}^0}{\delta w(q_1)} \right|_{w=z} = \frac{1}{\bar{L}^0[z]} \left. \frac{\delta \bar{L}^0}{\delta w(q_1)} \right|_{w=z} = \frac{1}{a};$$

and from (76), (77), and (75)

$$\begin{aligned} (83) \quad f_2(q_1, q_2) &= a^2 \left. \frac{\delta^2 \bar{L}^0}{\delta w(q_1) \delta w(q_2)} \right|_{w=z} = a^2 \bar{L}^0[z] \left\{ \frac{\delta \bar{M}^0}{\delta w(q_1)} \frac{\delta \bar{M}^0}{\delta w(q_2)} + \frac{\delta^2 \bar{M}^0}{\delta w(q_1) \delta w(q_2)} \right\} \bigg|_{w=z} \\ &= a^2 \left\{ \frac{1}{a^2} + \frac{\delta^2 \bar{M}^0}{\delta w(q_1) \delta w(q_2)} \right\} \bigg|_{w=z}. \end{aligned}$$

Thus from (78)

$$(84) \quad f_2(q_1, q_2) = 1 + a^2 \sum_{k=0}^{\infty} \frac{1}{k!} z^k \int \mathcal{E}_{k+2}^0(q_1, \dots, q_{k+2}) dq_3 \dots dq_{k+2},$$

and from (82)

$$(85) \quad 1 + \sum_{k=1}^{\infty} \frac{1}{k!} z^k \int \mathcal{E}_{k+1}^0(q, q_1, \dots, q_k) dq_1 \dots dq_k = \frac{1}{a}.$$

By virtue of the remark made at the end of the last paragraph, we see that the integrals appearing in (84) and (85) are convergent. If we set

$$(86) \quad b_k = \frac{1}{k!} \int \mathcal{E}_k^0(q, q_1, \dots, q_{k-1}) dq_1 \dots dq_{k-1}; \quad k = 2, 3, \dots; \quad b_1 = 1;$$

then (85) takes the form

$$(87) \quad v \sum_{k=1}^{\infty} k b_k z^k = 1.$$

The b_k are called 'cluster integrals' and are independent of q because the f_k^0 , and hence the \mathcal{E}_k^0 , are functions only of the coordinate differences. The quantity z is called the 'activity'. (84) expresses f_2 as a power series in the

activity, and the latter is related to the density $\frac{1}{v}$ by (87). In order to obtain an expression for f_2 as a power series in the density we assume that

$$(88) \quad z = \sum_{j=1}^{\infty} \frac{a_j}{v^j}$$

and insert in (87). One obtains easily that

$$(89) \quad z = \frac{1}{v} - \frac{2b_2}{v^2} + O\left(\frac{1}{v^3}\right),$$

and inserting in (84) we obtain

$$(90) \quad f_2(q_1, q_2) = 1 + g_2^0(q_1, q_2) + \frac{1}{v} \left[\int g_3^0(q_1, q_2, q_3) dq_3 - 2g_2^0(q_1, q_2) \int g_2^0(q_1, q_3) dq_3 \right] + O\left(\frac{1}{v^2}\right).$$

It can easily be shown that this result agrees with previously given expressions for f_2 , and can be used to obtain the virial expansion of the equation of state to order $\frac{1}{v}$. Formulas for f_s for $s > 2$ can be obtained by an obvious generalisation of the method used for f_2 . However, the solution of the functional differential equation, (55), is in principle already given by (71), where $\overline{L^0}$ is given by (61) and (70), and a is determined by (87).

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